

Electronic Supplementary Information

Formation of uniform colloidal spheres from Lignin, a renewable resource recovered from pulping spent liquor

Yong Qian^a, Yonghong Deng^{a}, Xueqing Qiu^{a*}, Hao Li^a, and Dongjie Yang^a*

^a School of Chemistry and Chemical Engineering, State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, People's Republic of China. Fax: +86 20-87114721; Tel: +86 20-87114722; E-mail: yhdeng08@163.com; xueqingqiu66@163.com.

Acetylation of alkali lignin. Purified alkali lignin sample was acetylated according to the acetylating procedures reported by Lu.¹ Specifically, 0.2g purified alkali lignin sample was added into 25ml mixed solution of acetyl bromide and acetic acid (5: 95 vol/vol). Then the mixtures were kept at 55 °C for 3 hours. Then the solvent was rotary evaporated for recycling under vacuum at 55 °C. The resulting ACL was immediately dissolved in THF for gel permeation chromatographic analysis (GPC) and colloid preparation.

In literatures, the acetylation of lignin has been done by using acetyl chloride² and acetic anhydride³ under the presence of catalyst, such as dimethyl acetamide, tri-ethyl amine, and pyridine. The reaction can be conducted under temperature as low as 0°C in a relatively short time. However, this process is environmentally unfriendly (not a green process) due to the involvement of catalyst. Alternatively, the acetylation of lignin could also be done without catalyst. In the absence of catalyst, higher temperature is required for this process, ranging from 70°C to 120°C, and requiring much longer reaction time.⁴ In other words, the process is high energy-consuming.

In this work, acetylation requires no catalyst, yet can be conducted under mild condition with short reaction time. Moreover, the acetic acid used in this reaction can be recycled after rotary evaporation. This method results in a more effective and greener process to acetylate lignin.

Influence of the water content on the degree of colloidization

The colloidal fraction of the ACL as a function of the water content can be estimated by using a method reported by previous work.⁵ Equation (1) in the article can be expressed as

$$C_0 = \exp [2.303(B - CWC) / A] \quad (1)$$

At CWC, the concentration of the ACL represents essentially the critical colloid concentration for colloid formation, which depends on the molecular weight of the ACL and the water content. For the ACL with a specific molecular weight, the higher the water content, the lower is the critical colloid concentration.

When the water content is beyond CWC, more and more ACL molecules associate to form colloidal spheres, and the concentration of the unassociated chains (C_{unass}) decreases. C_{unass} in colloidal dispersions is equal to the critical colloid concentration, which still obeys a relationship similar to Equation (1). Therefore, a similar equation can be obtained

$$C_{unass} = \exp [2.303(B - C_w) / A] \quad (2)$$

where C_w represents the water content (vol%) in the solution.

The colloidal fraction can be defined as a ratio of the associated chains to the total chains, $(C_0 - C_{unass})/C_0$. By combining the Equation 1 and 2, the following relationship can be obtained:

$$\begin{aligned} (C_0 - C_{unass}) / C_0 &= 1 - \exp [2.303(CWC - C_w) / A] \\ &= 1 - \exp [-2.303 \Delta H_2O / A] \end{aligned} \quad (3)$$

where ΔH_2O represents the water increment beyond CWC.

By using Equation 3, the change of $(C_0 - C_{unass})/C_0$ as a function of the H_2O increment can be calculated. The constant A can be obtained from the slope of the plot of CWC versus $\lg C_0$. A plot of $(C_0 - C_{unass})/C_0$ against the H_2O increment is shown in Figure S1, where the initial polymer concentration is 1.0 mg/mL and CWC is 44 vol%. When ΔH_2O is 23 vol% (i.e. the water content is 67 vol%), the percentage of ACL molecules involved in the clusters of the associated molecules is calculated to be

99%. Therefore, over the water content of 67 vol%, the amount of the “isolated” single molecules in the solution is negligible.

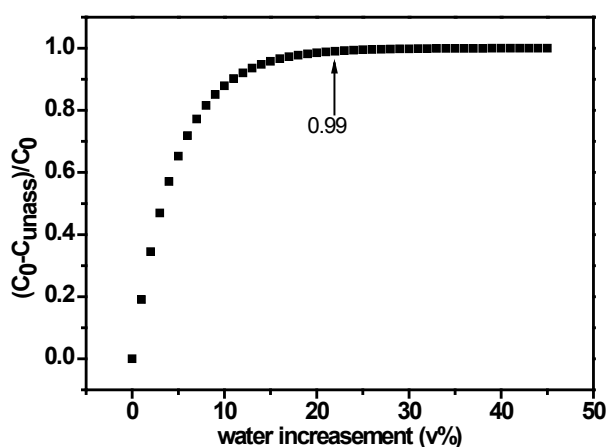


Figure S1 Fraction of the associated lignin molecules as a function of the water increment beyond CWC. Arrow indicates the water content where 99% lignin molecules are involved in the colloidal dispersion of the ACL.

Particle size of ACL colloidal spheres

Figure S2 shows the size distribution obtained from DLS measurement based on CONTIN algorithm. With cumulant analysis, the z-average hydrodynamic radius $\langle R_h \rangle$ is 110 nm with the polydispersity (μ_2/Γ^2) of 0.022. $\langle R_h \rangle$ can also be estimated from dynamic Zimm plot. The z-averaged diffusion coefficient $\langle D_z \rangle$ is estimated to be about $(2.32 \pm 0.09) \times 10^{-8}$ from dynamic Zimm plot of the apparent diffusion coefficients, and the $\langle R_h \rangle$ is calculated to be 106 ± 4 nm obtained from $\langle D_z \rangle$ based on the Stokes-Einstein relation. Obviously, $\langle R_h \rangle$ is slight larger than that of colloidal spheres observed by TEM.

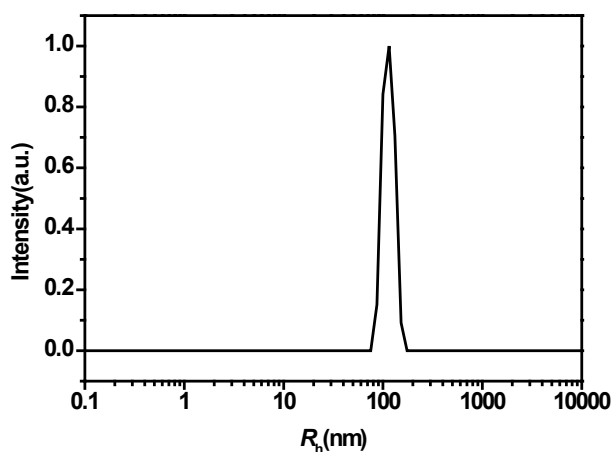


Fig. S2 Hydrodynamic radius (R_h) distribution of the ACL colloidal spheres based on CONTIN algorithm. The initial concentration of the ACL in THF was 1.0 mg mL^{-1} , and the detector angle of the DLS measurement is 60° .

Molecular weight of ACL colloids

The static light scattering (SLS) was used to determine the weight-average mass of the colloidal particles ($M_{w,p}$), the radius of gyration (R_g), and the second virial coefficient (A_2).⁶ According to the basic SLS theory, the particles scatter light according to the following relation:

$$\frac{KC}{R(\theta)} = \frac{1}{M_{w,p}} \left(1 + \frac{q^2 \langle R_g^2 \rangle}{3} \right) + 2A_2C \quad (4)$$

where K is the contrast factor, C is the concentration, θ is the angle at which scattering light is measured, $R(\theta)$ is the Rayleigh ratio at the angle of measurement, q is the scattering vector, A_2 is the second virial coefficient. Here $q = (4\pi n / \lambda_0) \sin(\theta/2)$, n is the refractive index of the solvent, λ_0 is the wavelength of the incident light, and θ is controlled to make sure $qR_g < 1$. Figure S3 shows the zimm plot of ACL colloidal nanoparticles in water at 25°C . The extrapolation of Kc/R to $c \rightarrow 0$ and $q \rightarrow 0$ leads to M_w . The slopes of $[KC/R(\theta)]_{c \rightarrow 0}$ vs q^2 and $[KC/R(\theta)]_{q \rightarrow 0}$ vs C lead to R_g and A_2 , respectively. M_w , R_g , and A_2 obtained from Figure S3 are $5.72 \times 10^8 \text{ g mol}^{-1}$, 82.7 nm , and $6.92 \times 10^{-9} \text{ mol cm}^3 \text{ g}^{-2}$, respectively.

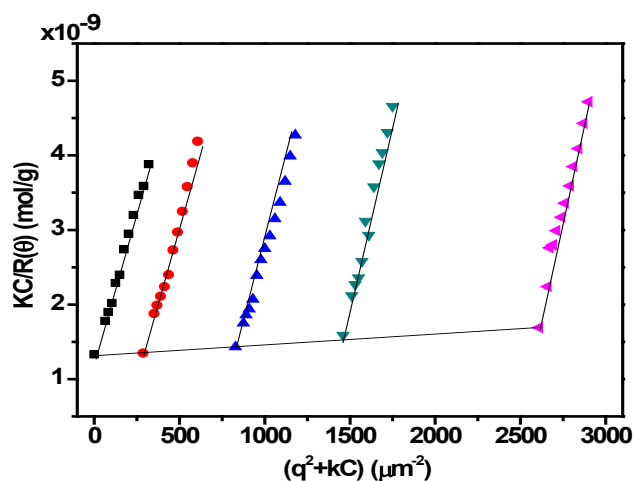


Fig. S3 Static Zimm plot of the ACL colloid nanoparticles in aqueous solution at 25°C, where C ranges from 9.89×10^{-6} to 7.52×10^{-5} g mL $^{-1}$, K is a constant for a given solution and temperature, and k is a constant to spread the plot.

Molecular weight of ACL single molecules

To calculate the aggregated number in each colloid, both M_w of the ACL colloids and that of ACL single molecules are needed to be known. Molecular weight of ACL single molecules is hard to be determined. M_w of ACL in THF was measured to be 4,200 by GPC with polydispersity index of 2.02. However, it was reported that M_w of the ACL dissolved in THF was 3.6×10^6 obtained from SLS measurement.² M_w measured by SLS (SLS_{Mw}) was much larger than that obtained by GPC (GPC_{Mw}).

The M_w difference between SLS_{Mw} and GPC_{Mw} are caused by three factors: aggregation effect; fluorescent emission; conformation differences between GPC standards (polystyrene) and the ACL molecules. Firstly, as reported by Merkle et.al., SLS_{Mw} of the ACL dissolved in THF was actually M_w of aggregates because the structure of the ACL had an average radius of gyration of 154 nm.² However, during GPC measurement, the elution of the mobile phase and shear force of the gel may make the ACL to remain a single-chain state when the sample pass through the gel column of GPC. Therefore, it is most possible that GPC_{Mw} is M_w of ACL single molecules, but SLS_{Mw} is M_w of ACL aggregates. Secondly, there is strong fluorescent emission from the ACL during SLS measurement, inducing SLS_{Mw} to be

overestimated; but fluorescent emission has no effect on GPC_{Mw} . Thirdly, GPC_{Mw} is a relative M_w because during GPC measurement polystyrene standard is used for a calibration curve. SLS measurement does not need any standard. The ACL has a more compact configuration than GPC standards (polystyrene), inducing GPC_{Mw} to be underestimated. Based on the above three reasons, SLS_{Mw} of the ACL dissolved in THF is much larger than GPC_{Mw} .

For absolute molecular weight determination of the ACL, SLS measurement can be used, but the influence of fluorescent emission and aggregation effect should be avoided. To avoid an overestimation of the molecular weight due to fluorescence, a high performance laser-line bandpass filter (Edmund, NT47-494) was placed between the sample solution and the photomultiplier to filter the fluorescence.⁷ In our previous paper, the aggregation effect of lignosulfonates can be eliminated by filtering the lignosulfonate solutions through a syringe filter with a suitable pore size.⁸ Here, we can use a similar method to eliminate the aggregation effect of ACL. Figure S4 shows the particle size distribution of the ACL/THF solution filtered by syringe filter with different pore sizes. Filtered by $0.45\ \mu\text{m}$ syringe filter, ACL exhibits a bimodal size distribution corresponding to a “fast mode” and “slow mode”.

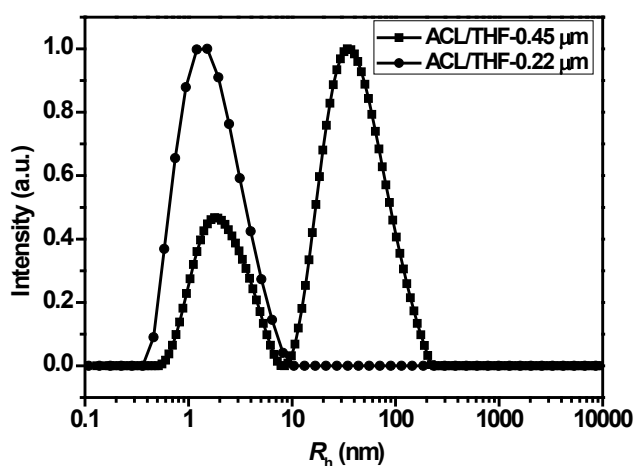


Fig.S4 R_h distribution of $1\ \text{mg mL}^{-1}$ ACL in THF based on CONTIN algorithm. Sample was filtered by syringe filter with different pore sizes, and the DLS measurement was performed at 60° .

The origin of the “fast mode” is attributed to the translational self-diffusion of the

single molecules, but that of the “slow mode” is in debate and controversy.⁹ The most possible reason for the “slow mode” occurring here is aggregation effects.⁹⁻¹⁰ When filtered by 0.22 μm syringe filter, ACL exhibits a monomodal size distribution corresponding to a “fast mode”, but the “slow mode” due to aggregation effect was disappeared. Therefore, the ACL in THF filtered by 0.22 μm syringe filter can be considered as the ACL single molecule, and SLS_{M_w} of the ACL molecules can be measured under this condition.

If the R_g of polymer molecules is less than $\lambda_0/20$, the scattered light would not show angle dependence. As shown in the insert plot of Figure S5, $KC/R(\theta)$ has little change with q^2 ; therefore, R_g cannot be obtained from the slopes of $[KC/R(\theta)]_{c \rightarrow 0}$ vs q^2 . As shown in Figure S5, the scattered light has a concentration dependence, so M_w of the ACL molecules can be calculated to be 5690 g mol^{-1} from the extrapolation of $KC/R(\theta)$ to $c \rightarrow 0$. The detail of $M_{w,m}$ determination for single molecules of lignin derivatives has been reported in the previous paper.⁸

Compared with the $M_{w,m}$ of ACL in THF measured by GPC, $M_{w,m}$ obtained from SLS is slight larger. This $M_{w,m}$ difference is caused by conformation difference between GPC standard and the ACL. Consequently, it is reasonable to believe that $M_{w,m}$ of ACL single molecules is actually 5690 g mol^{-1} .

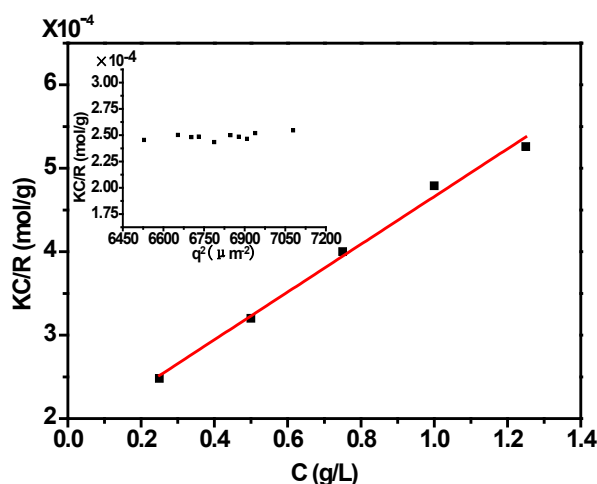


Fig.S5 Concentration dependence of $KC/R(\theta)$ for 0.25 g L^{-1} ACL solution in THF. Insert: $KC/R(\theta)$ vs. q^2 for 0.25 g L^{-1} ACL solution in THF. $M_{w,m}$ calculated from the extrapolation of $KC/R(\theta)$ to $C \rightarrow 0$.

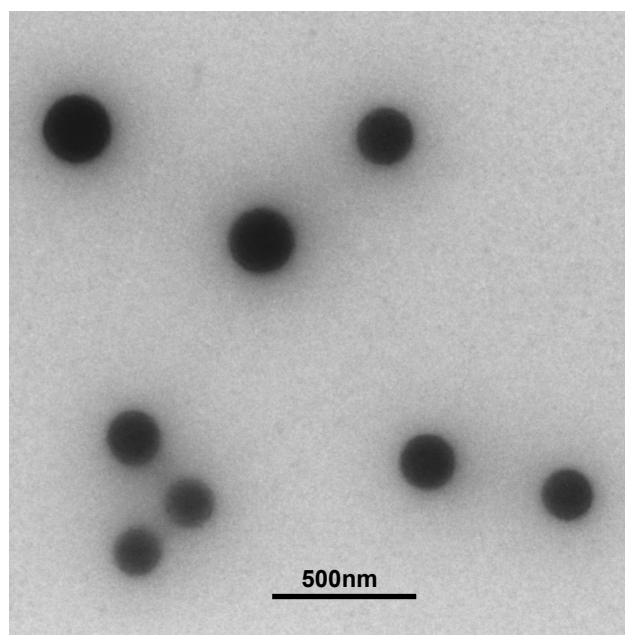


Fig.S6 TEM image of ACL colloidal spheres formed by adding alkali lignin aqueous solution into ACL/THF solution. The concentration of ACL/THF solution and alkali lignin aqueous solution were 1.0 mg ml^{-1} and 0.1 mg ml^{-1} respectively.

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